DIAGENESIS AND RESERVOIR QUALITY OF PANNONIAN LACUSTRINE DEPOSITS IN THE MAKÓ TROUGH, SE HUNGARY

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Introduction and goals

In the 2000s, the assumed presence of unconventional hydrocarbons, specifically basin-centred gas accumulations in the Makó Trough, had drawn the attention of several exploration companies (Badics et al., 2011). However, economic gas production has not been achieved (Badics et al, 2011) during exploration a vast amount of samples and data was collected. As a result, sedimentological architecture, geophysical and geochemical properties of these deposits become broadly known. Despite that, a detailed study on the diagenetic evolution of the deposits in the Makó Trough was not carried out.

Basin-centred gas accumulations are assigned as sandstone reservoirs of large extent but very low permeability (Law, 2002). These reservoirs are usually abnormally pressured and lacking a definitive gas-water contact (Law, 2002). Tight sandstones are reservoirs characterized with low porosity (<10%), low permeability (<0.1mD), complex pore structure and heterogeneity (Zou et al., 2012; Holditch, 2006; Wang et al., 2017; Lai et al., 2018).

Reservoir quality of sandstones are mainly controlled by primary depositional characteristics but can be significantly modify by diagenetic alterations (Morad et al., 2000, 2010; R. Worden and Burley, 2003; Schmid et al., 2004; Dutton, 2008; Ajdukiewicz and Lander, 2010; T. R. Taylor et al., 2010; Zhang et al., 2015; Lai et al., 2016). Diagenesis of unconventional tight sandstone reservoirs was recently studied in several basins, especially from China, Germany, and the United States of America (Higgs et al., 2007; Stroker et al., 2013; Becker et al., 2017; Li et al., 2017; Wüstefeld et al., 2017; Xiao et al., 2018; Lai et al., 2018; Ma et al., 2018; Busch et al., 2019; Fan et al., 2019; Kadkhodaie-Ilkhchi et al., 2019). Most significant processes, influencing reservoir quality are compaction, cementation of quartz and carbonates and clay mineral transformation reactions. Porosity enhancement in tight gas sandstones is usually connected to dissolution of unstable minerals and formation of secondary porosity. Preservation of porosity is generally assigned to formation of chlorite coats or early overpressure. Although, dissolution of unstable grains, and precipitation of clay minerals can enhance porosity, these processes led to the decrease of permeability (Li et al, 2017).

In case of tight gas sandstones, diagenetic facies is often used for characterization of reservoir quality (Fu et al., 2009; Lai et al., 2018). This concept is based on the determination of distribution of various diagenetic reactions and their impact in porosity and permeability evolution.

This study investigates the deeply buried Upper Miocene sandstones from the Makó Trough, focusing on diagenetic history and porosity evolution. The main objectives of the present research include: (1) petrographic and geochemical analysis of sandstones; (2) interpretation of paragenetic sequence and porosity evolution; (3) determining the origin of diagenetic minerals and the porosity; (4) reconstruct the fluid flow; (5) determining the factors influencing reservoir quality.

Materials and methods

Samples were taken from six wells from different structural settings. Two wells (M6, M7) are situated in the deepest central part of the Makó Trough. Four wells (Mcs1, K1, Szk1, BD1) are situated in marginal settings. Three formations of Pannonian age were sampled:

- Endrőd Formation
- Szolnok Formation
- Algyő Formation

15 core intervals from 6 wells were sampled from the Makó Trough in the depth interval of 2702 to 5475 m. 160 thin sections were analysed in optical microscope. All of these samples were impregnated with blue resin before thin sectioning in order to indicate porosity. Point counting was performed on 31 samples to investigate quantitative composition. 350 points per thin section were counted for sandstone composition.

A microscope equipped with a Hg vapour lamp and filters for blue light excitation (450–490 nm) was used to detect organic matter in the samples. The filter set was composed of a diachromatic beam splitter (510 nm) and a barrier filter (515 nm).

Cathodoluminescence (CL) studies were performed using a MAAS-Nuclide ELM-3 cold-cathode CL device (Measurement and Analysis Systems, Inc., Lowell, MA, US) on polished thin sections operating at 10 kV (Eötvös University).

Amray 1830i type Scanning Electron Microscope equipped with INCA Energy-dispersive X-ray spectrometer was used in the secondary electron (SE), backscatter electron (BSE) and cathodoluminescent (CL) modes on polished thin sections and in broken surfaces (Eötvös University). 21 samples were analyzed.

Fractured surfaces, coated with gold were studied on a FEI Inspect S Scanning Electron Microscope at the University of Vienna, Department of Geodynamics and Sedimentology.

The chemical composition of minerals was determined by a JXA-8530F type Electron Probe Microanalyzer in WDS mode (Slovak Academy of Sciences). Measurement conditions were the following: accelerating voltage of 15 kV, probe current 20 nA, beam diameter 5-10 μm, ZAF correction. 20 samples were analyzed.

X-ray diffraction method was used for identification of mineralogical composition in bulk rock samples and in separated clay fractions. A Panalytical PW 3040/60 X'Pert PRO diffractometer (CuKα radiation, 40 kV, 40 mA, step size 0.0167 s per step). at University of Vienna, Department of Geodynamics and Sedimentology was used.

For bulk mineralogy semi-quantitative estimation of the mineral constituents of the bulk samples were made following the method of Schultz (1964). In this method, the error limit is ± 10% for phases present in amounts >15% of the sample.

For clay-mineral analysis the <2 μm fractions were separated from the sandstones (Moore and Reynolds, 1997). Sandstones were crushed with a hammer, then disaggregated with diluted H_2O_2 and treated with a 400 W ultrasonic probe (2- 3 min). Carbonate containing samples were treated with 0.1 $_M$ EDTA solution (pH 4.5) and washed with distilled water (Glover, 1961, Kohler and Wewer, 1980). Size fractionation was accomplished by timed sedimentation (Stokes'size fraction).

Oriented XRD mounts were prepared by pipetting the suspensions (7 mg sample in 1 ml of distilled water) onto glass slides and analyzed after air drying. Furthermore, the clay fractions were saturated with K^+ or Mg^{2+} ions, followed by ethylene glycol or glycerol saturation or heating (550°C), in order to recognize expandable or heat-sensitive clay minerals (Moore and Reynolds, 1997).

The <0.2 μm fractions were separated by timed centrifugation. The resulting suspensions were concentrated by evaporation and the wet samples were freeze dried. Oriented preparations for XRD were made by dispersing ~5 mg clay separate in 1ml of water, pipetting the suspension onto a glass slide and dried at room temperature. Oriented XRD mounts were solvated with ethylene glycol at 60 ^oC for 12 h.

In mixed-layer phases the percentage of illite was determined by the 2Θ difference values of the peak positions 001/002 and 002/003 of the illite/smectite mixed layer peaks (Moore and Reynolds, 1997).

Polished sections of 1-cm-thickness were sampled by a binocular based computer controlled micro-mill, which allowed the separation of carbonate phases.

Stable carbon and oxygen isotope analyses were carried out on a MAT253 gas isotope mass spectrometer (Thermo Scientific) coupled to a Kiel IV (Thermo Scientific) automatic preparation line. The carbonates were digested in H_3PO_4 at 70^{o}C in a vacuum following the method of McCrea (1950). The measurements were carried out at the Geological Institute of the Slovak Academy of Sciences, Banská Bystrica. The results are expressed in δ-notation on the Vienna PDB standard. 35 samples were analyzed.

Results, theses of the dissertation

1. The analysed deposits in Endrőd, Szolnok and Algyő Formations of the Makó Trough consist of fine to medium sandstones of poorly to moderately sorted grains and were classified as litharenites and fedspatic litharenites (sensu Folk, 1968). Detrital grains in each formation consist of quartz, feldspar, mica, sedimentary- and metamorphic rock fragments. A difference in composition was observed: in the Algyő Formation the quantity of quartz is higher while in Szolnok and Endrőd Formations the quantity of feldspar and rock fragments are higher. Diagenetic minerals are pyrite, calcite, ankerite, albite and quartz. Detrital and diagenetic clay minerals are encountered as kaolinite, dickite, mixed-layer smectite/illite, discrete illite and chlorite.
2. The observed diagenetic minerals and processes were interpreted according to the model of Morad (2000). In the realm of Eogenesisis mechanical compaction, formation of clay coats and framboidal pyrite were the most significant processes. In the Endrőd and Szolnok Formations additionally pre-compactional calcite (Cal1E, Cal1Sz) precipitated.

3. In the early stage of mesogenesis (Mesogenesis I.), various diagenetic processes, such as the formation of ankerite, albitization of feldspar, illitization of smectite, quartz cementation and chlorite formation occurred. Post-compactional calcite (Cal2E, Cal2Sz, Cal3A) also precipitated in this zone. In late stage of mesogenesis (Mesogenesis II.) in the Algyő Formation, kaolinite and dickite were formed. Additionally, the dissolution of detrital and mesogenetic minerals, such as Cal3A calcite and formation of secondary porosity with residual bitumen also occurred.
4. Based on petrographic features and geochemical data various calcite phases of different origin were distinguished. Pre-compactional calcite phases (Cal1E and Cal1Sz) being present in Endrőd and Szolnok Formations are poor in $FeCO_3$+ $MnCO_3$ and moderately rich in $MgCO_3$. According to stable isotopic data, these phases were formed in a temperature below 50^{o}C. Post compactional calcite phases in Endrőd and Szolnok Formation (Cal2E and Cal2Sz) post-dates albite and ankerite, whereas in Algyő Formation such calcite (Cal3A) also post-dates quartz. Post-compactional calcite is $MgCO_3$ rich in Endrőd Formation, $FeCO_3$+$MnCO_3$ content is moderate. Post-compactional calcite in Szolnok Formation is poor in $MgCO_3$, whereas its $FeCO_3$+$MnCO_3$ contents are highly variable. Cal3A in Algyő Formation exhibits a high variability in $FeCO_3$+$MnCO_3$ and moderate variability in $MgCO_3$ content. Based on stable isotope data these phases formed in 55 to 65^{o}C in Endrőd Formation, 65 to 70^{o}C in Szolnok Formation and 70 to 85^{o}C in Algyő Formation.
5. Detailed clay mineral analyses were encountered in the depth interval of 2700 to 4000 m. The proportion of illite in mixed-layer illite/smectite gradually increases with depth. In the deepest part of the analysed section only discrete illite was found. The transition from R1 to R3 ordering was observed at 3400 m depth.
6. Transformation of kaolinite to dickite was only detected in Algyő Formation, which can be explained by the fact that this reaction can only take place in open systems (high permeability reservoirs) (cf Marfil et al, 2003 and Mansurbeg et al. 2012). As a consequence, in Szolnok Formation the lack of porosity and permeability prevented this reaction in late diagenesis.
7. Burial history and porosity evolution of the analyzed sandstones was reconstructed. In the early stage of Eogenesis, sandstones lost their porosity due to pre-compactional calcite (Cal1E and Cl2E) and mechanical compaction. Precipitation of clay minerals also contributed to porosity lost in Endrőd and Szolnok Formations. At this stage, diagenetic minerals were originated from internal sources.
8. After the deposition of Szolnok Formation, Mesogenesis I. started in Endrőd Formation. Precipitation of cement, such as albite, ankerite, quartz, clay minerals and Cal2E lead to the destruction of porosity. Increasing amount of Cal2 from the centre to the margins of the basin and increasing formation temperature with decreasing depth (from Endrőd to Algyő Formation) suggest that these phases were sourced from compactional fluid flow. Such flow expelled from Endrőd and Szolnok Formations. Some of the Cal2 paheses originate from internal sources.
9. During the deposition of the Algyő Formation, the alteration processes of Mesogenesis I. took place in the Szolnok Formation, whereas the alteration processes of Mesogenesis II. occurred in the Endrőd Formation. Meantime, the Endrőd Formation

reached the oil window and the Szolnok Formation lost the majority of its porosity in the zone of Mesogenesis I.. As a result, from the overpressured Endrőd Formation hydrocarbon-bearing fluids entered to the basement, where paleo-meteoric fluids were already present. This is in accordance with the observations of Juhász et al (2002), M. Tóth et al. (2007) and Fiser-Nagy (2013).

10. Later on, external fluids entered the Algyő Formation, causing dissolution and alteration of feldspar to kaolinite. Those external fluids likely originated from the paleo-meteoric fluids and formational fluids of Endrőd Formation from the basement. As a result, in several layers of Algyő Formation secondary porosity was formed. Based on the residual bitumen, found in secondary porosity, the dissolution took place in a pore-fluid containing hydrocarbons.
11. Reservoir quality of the sandstones was most significantly influenced by compaction and cementation by various mineral phases. Consequently, the majority of the analysed sandstones lost their porosity and became tightly cemented of poor reservoir quality. No porosity-preserving processes were observed. A late event of dissolution and formation secondary porosity was identified in the Algyő Formation, causing the enhancement of reservoir quality.

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